

**Potential Applications for
Liquid Silicon Melt Infiltrated (LSI) Composites
to the High-Temperature Sulfur-Iodine (S-I) Process**

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Summary

The report presents potential applications for Silicon Melt Infiltrated (LSI) ceramic composites to the high-temperature Sulfur-Iodine (S-I) process for the thermo-chemical production of hydrogen. A novel concept for hydrogen production has been proposed by the US Department of Energy (DOE), which combines the use of heat derived from a nuclear power plant (a Generation IV reactor) for the production of hydrogen in a thermo-chemical plant. Similar technology could also be applied to hydrogen production from solar power towers. Present activities concentrate on the development of heat exchangers, which are one of the key components of the concept. Novel plate-type compact HXs with high power density are proposed, which are based on novel channel designs. The designs for intermediate heat exchangers (IHX) as well as decomposers for the splitting of sulfuric acid are under investigation. Helium or alternatively liquid salts are under consideration as intermediate heat transfer fluids. Within the chemical plant components like boilers and process vessels are needed, which must withstand severe chemical attack by both liquid and gas phases.

For these novel high temperature applications (600-1000 °C), in combination with corrosive environments, ceramics are under investigation. SiC based ceramics are the first choice, since they have a high thermal conductivity, a low coefficient of thermal expansion and high strength. In particular, C/C-SiC or C/SiSiC ceramics have improved fracture toughness based on short carbon fibres or 2D carbon fabrics and can overcome the brittleness of monolithic SiC ceramics, and therefore provide a potentially attractive approach. Because carbon can be oxidised at temperatures of about $> 400\text{ }^{\circ}\text{C}$, there will be a strong need for an additional oxidation protection coating (OPC), e.g. CVD-SiC. The oxidation of silicon and SiC must be also investigated when the material will be used in long-term (> 1000 hours). Because the composites will be used in severe corrosion environments like high temperature sulfuric or phosphoric acid, an additional environmental barrier coating (EBC) must be applied.

Three main S-I application fields for LSI composites are identified and proposed. These applications cover boilers and vessels within the thermo-chemical plant and compact heat exchangers for heat-transfer in the intermediate loop or as chemical reactors. It is also worthwhile to examine the use of ceramic tubes for the transfer of liquid salts from the nuclear power plant to the thermo-chemical plant.

In the first step it is recommended to investigate at least three different types of available LSI composites in corrosive environments. For these preliminary screening experiments small samples, 30-50 mm in diameter, with and without surface coatings will be sufficient. The material stability at least up to 1000 hours must be demonstrated. After these tests prototype components can be preferably manufactured by using an autoclave or Resin Transfer Molding (RTM) technique.

The development of plate-type heat exchangers require the use of a highly gas-tight composite, so that the use short fibre reinforced material (B1) appears to be most promising. This material can most probably be molded in the desired net-shape design to create millimetre-scale flow channels and other flow geometries, as required for the specific heat transfer and chemical process need. Since the composite fabrication is in an early stage, research for another two years must be done to identify the appropriate processing parameters and to prove the feasibility of the technology. The component development must be accompanied by permeability measurements in order to test the reliability of the bonds between the laminated plates.

1 Nuclear Hydrogen Initiative (NHI)

Due to the increasing energy demand there is strong need for renewable energy opportunities as an alternative to fossil fuel. The US governmental programs support the development of high temperature heat exchangers (HTHX) for hydrogen production and electrical energy conversion. The projects also support the development of Generation IV (Gen IV) reactors, since nuclear energy is emission free and can provide the high temperatures required for water splitting technologies. It is an overall objective to reduce fossil fuel consumption by supplying non-fossil hydrogen to oil refineries, and ultimately to replace fossil fuel through hydrogen, e.g. for hydrogen-fuel vehicles, by using efficient production technologies. There are two approaches for the production of hydrogen using nuclear energy: thermally assisted electrolysis and thermo chemical processes. Electrolysis is the splitting of water molecules by using electricity. The efficiency of the complete process to generate hydrogen is only about 25 % due to the relatively low thermal efficiency of current reactors in producing electricity (~33 %), and the finite efficiency of electrolysis. The efficiency of direct electrolysis could be probably increased up to 45 % with higher thermal efficiencies from HT nuclear power plants. This motivates the investigation of methods that could have significantly higher efficiency, in particular high-temperature electrolysis and thermo-chemical cycles.

2 High-temperature nuclear power plants and heat transfer

Very High Temperature Reactors (VHTR's) have high priority among the U.S. reactor concepts of Next Generation Nuclear Power Plants (NGNP), since they can operate at very high temperatures (above 850 °C) producing 600-2400 megawatts of thermal power [1]. The materials used in the VHTR must withstand very high temperature, intense neutron radiation and corrosive environments. For high-temperature intermediate heat transport liquid salts are a desirable heat transfer fluid due to their high volumetric heat capacity. For this purpose there will be a need for a long pipe of some 100 meters or more for the transport of this liquid-salt coolant from the nuclear power plant to the IHX or thermo-chemical plant. For this purpose efficient heat transfer fluids are required. Besides helium, primary molten (or liquid) fluoride and chloride salt coolants are the first choice and therefore under investigation [2]. The material screening focuses on salt compositions with high chemical stability for

$T > 800\text{ }^{\circ}\text{C}$, melting points $T < 525\text{ }^{\circ}\text{C}$, low vapor pressure, and compatibility with alloys, graphite and ceramics as needed for the heat transfer loop. Impurities, temperature gradients and activity gradients might increase liquid salt corrosion problems. In addition to the LiF/NaF/KF salt flinak, future high temperature corrosion tests will also study LiCl-KCl-MgCl₂ salts, since they also have the potential to meet these basic requirements and are very inexpensive [3].

3 High-temperature compact heat exchanger (HX) development

3.1 Design aspects for ceramic HX modules

Plate-type HX with small flow channels provide a good approach for constructing an IHX because high power density can be obtained. The off-set fin (OSF) plate design is proposed, which should enable a very large heat transfer area density and an effective counter current flow. The complete HX module is based on alternating liquid salt and helium plates, which are joined together. The channels should not exceed 3 mm in height, 10 mm in length, and 3 mm in width, respectively. The total HX dimension should not exceed $0.9 \times 1 \times 1\text{ m}^3$. Due to the compact design low stresses were found through FEM simulations, so that safety factors of 6 to 8 could be concluded [4].

Alternatively, different shell HX, plate HX, and decomposer designs with different complexity were carried out by Ceramtec Inc. in collaboration with UNLV [5]. All these designs can be processed by using the Laminated Object Manufacturing (LOM). The final design has to be compact and reliable. Single channel, hexagonal, and diamond-like channel designs were proposed with a channel offset of about 50-100 %. The channel designs were investigated and optimized by pressure measurements using pressure transducers [6, 7].

3.2 Material requirements for plate-type HX

HX are the key energy conversion components for thermally driven hydrogen production [8]. The success of the Gen IV project relies critically on the design and performance of these system components. Promising material candidates cover HT nickel-based alloys, HT ferritic steels as well as advanced carbon and SiC

composites. Within the ongoing DOE project such materials for HX components should be identified and tested.

The primary coolant of the NGNP reactor will be helium. Advanced reactors, after the NGNP, may also be designed to use liquid salt as the primary coolant. The intermediate HX (IHX) would be preferably then consists of helium-to-liquid-salt or helium-to-helium modules housed within a gas-tight vessel. It operates at temperatures from 600-1000 °C. For the helium to liquid-salt option, the IHX operates with a pressure difference from 6 to 8 MPa, while for the helium-to-helium option the IHX operates in pressure balance and the process heat exchangers must accommodate the pressure differential. The following coolants and process fluents for HXs are under consideration:

- * *Helium*: Primary coolant for near term demonstration, heat transfer fluid
- * *Liquid salts*: Fluoride or chloride based salts with high heat capacity for the intermediate coolant, and possibly primary coolant
- * *Lead-Bismuth*: Liquid metal for heat transfer due to the high boiling point
- * *Sulfuric acid*: Primary process fluid, creates aggressively oxidizing conditions
- * *Phosphoric acid*: In contact to HI₂ to separate I₂ from HI and water
- * *Hydrogen Iodide*: Interaction of solution at the decomposition temperature (450 °C)
- * *Hydrogen*: Hydrogen embrittlement of materials must be considered

Another critical area of the S-I cycle is the point of interaction between the heat transfer medium and the sulphuric acid decomposition section. An IHX design is required, which optimizes thermal efficiency and is capable of withstanding the corrosive environment.

If such a HX is primarily used as a decomposer for corrosive sulphuric acid, it should maintain appropriate conditions for the chemical splitting reactions at $T > 850\text{ }^{\circ}\text{C}$. The materials must be gas-tight, corrosion resistant and should exhibit high fracture and creep strength. It must be capable to work in the temperature range of 800-1000 °C. The material must almost maintain full mechanical strength in this temperature range. The materials must be also cheap and should be preferably fabricated in net-shape design. Coatings must be applied to achieve gas hermeticity and corrosion resistance against the S-I feed components like H₂SO₄ or SO₃. The material should be also thermo-shock resistant due to thermal transients might be occur when the flow of process fluid or coolant is stopped. The temperature gradients between the inlet and outlet could be up to 400 °C so that there will be a strong need for a

compact HX design with a low stress level and ceramics with an improved fracture toughness [4].

3.3 Pre-tests with potential HX materials

Different monolithic ceramics are currently under investigation at Ceramatec Inc. These ceramics cover primarily SiC, Si₃N₄, Al₂O₃ and others. All of these ceramics seem to be feasible and selection will be mainly based on cost and performance criteria.

High pressure tests with helium at UC Berkeley showed, that especially CVD coated C/SiC samples could keep hermeticity under high pressure and stress well beyond the working pressure differences and stresses expected in a ceramic compact plate-type HX [4].

4 Sulfur-Iodine (S-I) cycle

Two of the most promising thermo-chemical cycles are the sulfur-iodine (S-I) cycle (General Atomic (GA) cycle) and the hybrid sulfuric acid cycle (Westinghouse cycle). Both have in common the decomposition of sulfuric acid. The on-going investigations concentrate on the hydrogen production by using the S-I cycle which is a thermo-chemical water splitting cycle due to the thermal efficiency of about 50 %. The key endothermic reactions (1-3) of the thermo-chemical process sum to create the dissociation of water (4). The reactions can be seen below. The reactants are highly reactive and occur in various states, mainly liquid or gas. It is foreseen that a small pilot plant for H₂-production with an output of ~ 200-1000 l/h will be constructed in 2007 at GA to demonstrate the technical feasibility of the process. For this purpose the hardware for step 1 will be provided by CEA, the H₂SO₄ decomposer by Sandia, and the HI boiler by GA [9]. For this prototype demonstrator some components have to be made of expensive Hastelloys or tantalum, especially when they are in contact with extremely corrosive chemicals like HI_x. The prototype H₂SO₄ decomposer will be constructed with a tube-in-tube design using commercial SiSiC ceramic as the outer tube.

All of the reactants are regenerated and recycled, which can be energy consuming. Some fluid separation steps can be derived from table 1. In reality the chemistry is more complex.

Thermochemical reactions:

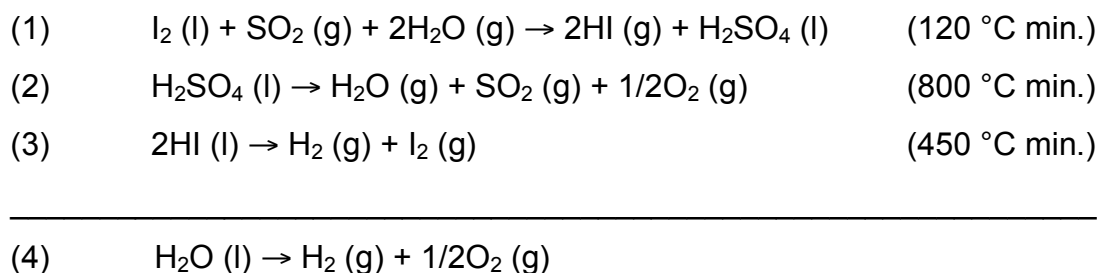


Table 1. Main fluid separation steps in the S-I cycle at General Atomics (Bunsen Process).

Environments	Contaminants	Chemical content
Iodine separation, 140 °C	H ₂ SO ₄ in HI from section 1	H ₂ SO ₄ , HI, I ₂ ; H ₂ O, SO ₂
Phosphoric acid conc., 250 °C	HI and I ₂ from distillation	87 % H ₃ PO ₄ , HI, H ₂ O, I ₂
HI decomposition, 450 °C		H ₂ , I ₂ , HI

4.1 The role of catalysts

In regard to a higher efficiency of the splitting reaction of SO₃ into SO₂ at temperatures of about 750-900 °C Pt/TiO₂ catalysts were investigated. The activity of the catalyst increase with the BET area, but the stability decreases. The catalysts were dispersed as nanoparticles on the surface of various ceramic substrates (SiO₂, TiO₂, Al₂O₃). During the long-term tests using catalysts like Pt, Pd, Pt/Ru, Pt/Rh, and Pt/Pd (0.1-1.0 wt%), growth in particle size was observed and there were smaller particles left after the tests were completed. The deactivation of the Pt is probably due to sintering, oxidation and vaporization. Since the decomposition process provides extremely harsh environments for catalysts and base materials stability, highly and long-term active catalysts have not yet been identified. Novel approaches will be studied to use complex metal oxides like CuCr₂O₄, NiCr₂O₄, FeTiO₃, which are probably more stable at high temperatures. [10]. It is also proposed by researchers from KIST, Korea that copper-oxides with spinell structures are the most promising catalysts for the sulphur acid decomposition [11].

4.2 Corrosion issues and pre-testing

There is a series of chemical products relating to the S-I cycle, so that all used materials have to withstand severe environments during operation as can be seen from table 2. The basic components, which will be in direct contact with corrosive

liquids or gases are tubes, vessels, boilers, and heat-exchangers. Post-investigations of the materials must be concentrated on the microstructural changes and their corrosion and oxidation behavior in order to predict the lifetime of the components.

Table 2. Corrosion test matrix for materials w/wo coating within S-I cycle.

Environments	Temperature	Responsibility
H ₂ SO ₄ -Decomp., SO ₃ /SO ₂	850 °C	SNL
HI _x -Decomp.	140 °C	GA
H ₃ PO ₄ (95 %) Conc.	250 °C	GA
Iodine Sep.	450 °C	GA
Liquid salts	900 °C	ORNL

Corrosion tests with sulfur acid decomposition inside SiC based ceramic HX channels were already performed by Ceramtec Inc. from 450 °C up to 900 °C under exposure of steam, H₂SO₄ (gas), oxygen and nitrogen [12]. The exposure time was up to 1000 h. Flow rates of about 2.0 sccm were chosen in liquid (acid/water mix) and 150 sccm in air. Different mole fractions were maintained: water 30, 60 %, H₂SO₄: 30, 60 %, oxygen: 29.5 %, nitrogen: 0.5, 8 %. Results from 1000 h exposure of SiC specimens showed only little effect on the flexural strength and low weight gain. A decrease in corrosion rate was observed with exposure time. Slightly oxidation could be determined but no excessive damage occurred. The silica scale showed little contamination by K, Na, Ca, and Cl. From these results it could be concluded that the corrosion resistance of SiC-based ceramics is most likely controlled by the stability of the silica scale during operation. Crack or flaw healing through the silica scale can be assumed, because the flexure strength was slightly increased.

Corrosion experiments related to the Iodine separation (HI_x-H₃PO₄) and H₃PO₄ separation (85-96 wt% H₃PO₄-HI-H₂O) were performed by General Atomics (GA) at low temperatures of 140 °C and 250 °C, respectively. Especially tantalum and SiC based materials showed no sign of corrosion after the tests with exposure times ranging 120-1000 hours. Tantalum based materials were superior. These tests are continuing. A weight gain could often be observed due to a phosphate layer that was attached on the specimen's surfaces [13].

5 Liquid Silicon Infiltrated (LSI) composites

Ceramic matrix composites (CMCs) have been investigated for nearly 18 years by the German Aerospace Center (DLR), especially for space and aeronautics applications. The motivation for the development was to overcome the brittleness of monolithic ceramics by using fibres as a reinforcement phase. Since then C/C-SiC composites, derived from carbon/carbon (C/C) preforms, can be manufactured with a high variability of properties and are now commercially available [14]. The materials can be manufactured with high reproducibility, due to stable fabrication process and quality inspection. The typical processing includes three steps: CFRP manufacture, pyrolysis and Si-melt infiltration. The properties of Si-infiltrated ceramic composites are shown in table 3 and basically determined by the microstructure (fig. 1). Different types of composites are known:

- * *XB composite*: The XB composite is based on high tenacity fibres (HTA from Tenax) and a liquid phenolic resin, providing a very high char yield exceeding 60 m%. The 2D fabrics are used as received without any further modification, except a drying step at 100 °C for one hour in order to remove absorbed moisture. The use of C-fibres yield dense segments of C/C-fibre bundles after pyrolysis, providing load bearing C-fibres within a more or less weakly bonded carbon matrix, which protects the fibre bundles from being siliconized. During pyrolysis only a few distinct microcracks formed within the weak carbon matrix, which is the result of the high fibre-matrix bonding. These type of composite as well as XD, XT, and XG composites can be preferably fabricated by RTM or autoclave techniques.

- * *XD composite*: If a fibre pre-treatment prior to CFRP manufacture is performed at elevated temperatures, the microstructure of C/C-SiC could be significantly changed. With increasing temperature of fibre pre-treatment, ranging from 600 to 1700 °C, the formation of dense C/C-segments is hindered due to lower chemical bonds between the fibres and the carbon matrix. Consequently, more and more randomly oriented cracks are formed during the pyrolysis step, allowing an increasing amount of silicon to enter these crack paths and decreasing the amount of load bearing carbon fibres.

- * *XT composite*: Using moderate fibre pre-treatment temperature (e.g. 600 °C) in combination with intermediate modulus fibres (T800, from Toray), the mechanical strength values could be significantly increased compared with XB composites.

- * *XG composite*: If different layers of thermally pre-treated 2D fabrics are combined in a symmetrical lay-up within one composite, a gradient composite can be achieved.

The higher the pre-treatment temperature the higher will be the conversion rate of carbon fibres inside the composite during the final Si-infiltration.

* *SF composite*: To obtain this type of composite inexpensive short carbon fibres (HTA from Tenax) with different lengths of 5-40 mm are mixed with phenolic resin (powder or liquid) to homogeneous compounds. The compounds are then molded by axial pressing. This is the preferred technique to accomplish net-shape components in series production at low costs. The series production of automobile brake discs is based on this composite type revealing a gradient microstructure.

* *B1 composite*: The B1 composite type is a non-typical CMC, since it is quasiisotropic and the properties are not dominated by the carbon fibres [15]. It can be performed by using a mixture of very short carbon fibres (lengths < 1 mm), phenolic powder resin, and inexpensive wood powders. The compound can be molded into homogenous plates with thicknesses up to 60 mm as well as net-shape parts. The microstructure is crack free and therefore gas-tight. Compared to other CMCs the fibre content is only about 20-30 vol%. On the other hand the SiC and silicon content is high and therefore the material has a much more higher brittleness. This composite type shows a very high Young's modulus and strength, which makes it an interesting candidate for lightweight structures with high stiffness.

Table 3. Properties and composition of Si-infiltrated composites.

	Unit	XB	XD	XT	XG	SF	B1
Density	g/cm ³	1.9	2.3	1.9	2.1	2.1-2.3	2.8
Open porosity	Vol%	3.5	2.8	3.7	<5	1-3	<1
Flexural strength	MPa	160	80	300	65-80	90-140	185
Tensile strength	MPa	80	30	190	31	n.d.	n.d.
Strain to failure (ϵ)	-	0.15	0.04	0.35	0.15-0.2	n.d.	n.d.
Young's Modulus	GPa	60	100	60	41	50-70	294
Th. Cond. (λ)	W/mK	10	19	13	19	25-30	45
CTE (α)	10 ⁻⁶ K ⁻¹	2.5-6.5	4.5	2.5	n.d.	1.0-4.0	2.6
Si-content	M%	6	2	5	3	4	33
SiC-content	M%	33	61	31	47	44	59
C-content	M%	61	37	64	50	52	8

(n.d. = not determined)

All properties were determined at RT from DLR prototype materials, which were performed in-house. The density and porosity were determined by the Archimedes

method. The flexural strength was performed by using the 3-point bending test. The composition was determined by using HNO₃ oxidation/HF etching and complete final carbon oxidation at 1000 °C. The CTE and λ -values were derived from cut specimens perpendicular to the fibre elongation.

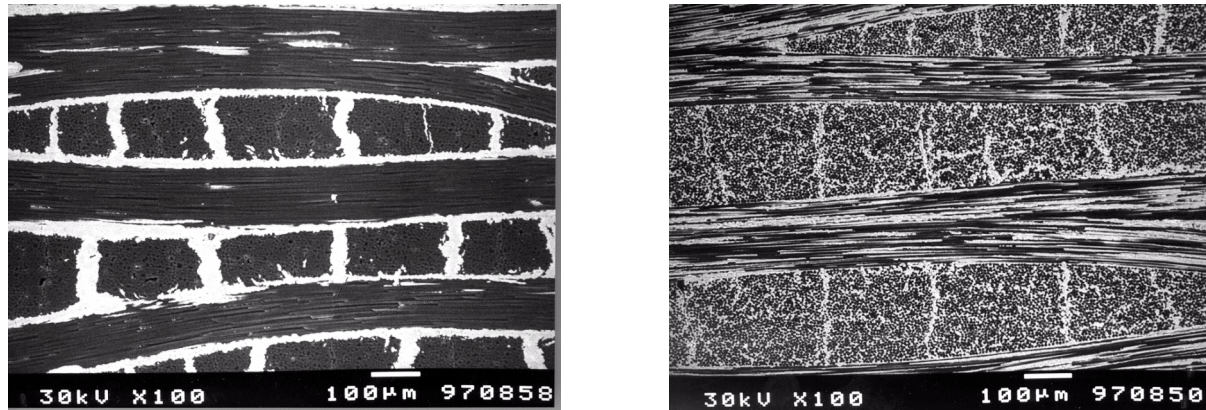


Fig. 1. Typical microstructures of Si-infiltrated ceramic composites (C/C-SiC) under SEM. LSI ceramic composite type XB (left), XD (right), bright phases: silicon/SiC, dark phase: carbon.

5.1 Fabrication and availability of LSI composites

All proposed Si-infiltrated ceramics are based on a three step process including CFRP, pyrolysis, and final Si-infiltration. The differences lie especially in the shaping of the basic CFRP bodies and the choice of raw materials, which primarily influence the microstructure and therefore the properties. The CFRP fabrication requires pressures of about 1-20 bar and curing temperatures of about 200-250 °C. The following CFRP fabrication (fig. 2) methods are in use at DLR:

- * *Resin Transfer Molding (RTM)*: High expense in outer steel molds and inner cores, closed molds required. Use of dry carbon fabrics. Preferred method for plates, tubes, and small complex 3D net-shape parts (e.g. radomes).
- * *Autoclave technique*: Low expense in polymer molds (only negatives as cores) or no mold is required. Use of 2D carbon prepregs. Preferred method for large plates and big 3D complex net-shape parts (e.g. nose-caps).
- * *Net-shape molding* through axial pressing: Average expense in steel molds, closed molds required. Use of 2D carbon prepregs or short fibre based compounds. Preferred method for plate and disc fabrication.

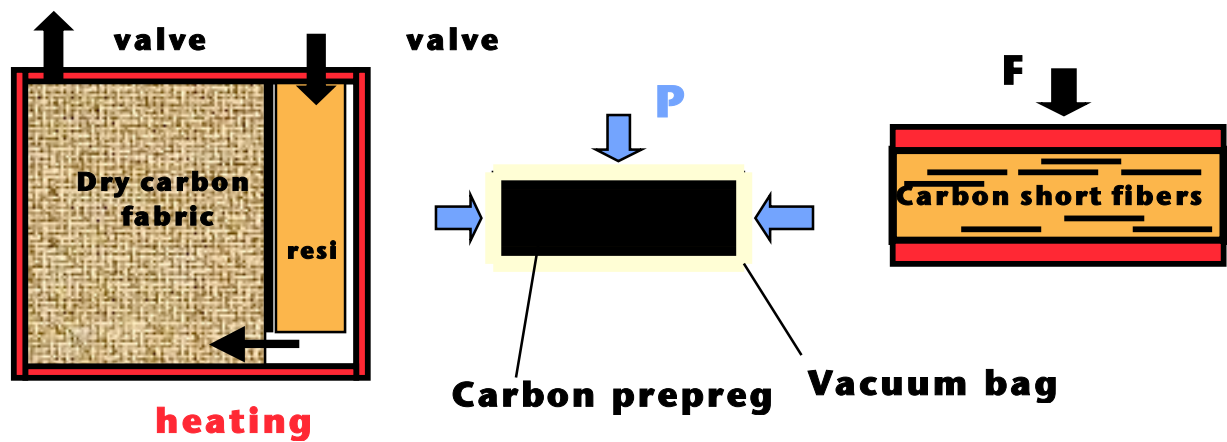


Fig. 2. Schematic representation of common CFRP fabrication methods using phenolic resin and carbon fibres as raw materials. From left to right: RTM, autoclave, hot molding.

Due to the limited size and volume of the present high temperature furnaces (pyrolysis and siliconization) CFRP parts with maximum dimensions of about 800-900 mm were fabricated. However, the methods allow the manufacture of bigger parts. Components with thicknesses > 5 mm must be processed very carefully, because delaminations might occur due to weak fibre-matrix bonding. Very complex shaped parts can also be performed by joining C/C semi-finished products, preferentially after pyrolysis, e.g. tubes with flanges (fig. 3, 4). To obtain accurate in-situ joinings the single parts must be machined with low tolerances (± 0.2 mm).



Fig. 3. Semi-finished parts made from carbon/carbon after machining to be ready for joining.

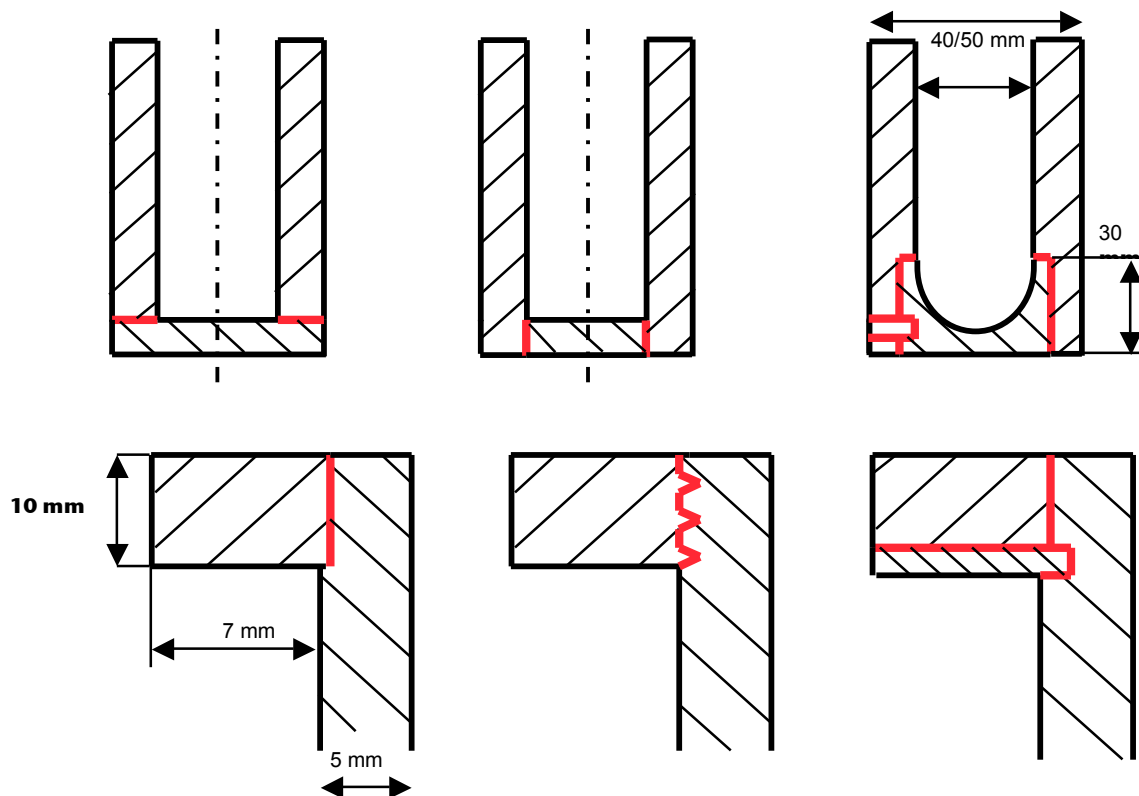


Fig. 4. Design options for tube-to-flange or tube-to-end-cap joining in the C/C state prior to liquid Si-melt infiltration [16].

5.2 Applications for LSI composites

Si-infiltrated composites have been investigated primarily for short-term use (seconds to some minutes) in space. In the last years the LSI materials have been investigated increasingly for long-term (2-10 years) applications.

- * For structural, very short term application where a high safety factor is needed, e.g. space applications, XB or XT is the best choice, since both materials exhibit the highest strength of all available C/C-SiC types.
- * Friction applications are mainly based on composite XG and SF where a high ceramic content near the surface is required to maintain low wear and high friction coefficients.
- * B1 composite is promised to be the best candidate in terms of low gas-tightness. Other C/C-SiC can hardly be used if very low permeability is needed, e.g. heat-exchangers, since the open-porosity is approx. > 3 vol%.

- * Most of the C/C-SiC composites show poor oxidation resistance. This starts at about 400 °C and therefore the composites need an additional coating when used in air or combustion environments (e.g. gas turbine components).
- * SF or B1 ceramics can be used for applications where high stiffness, high thermal conductivity or low oxidation is required, due to the high ceramic content.
- * For the long-term use of any LSI composite at high temperature protection surface coatings will mostly be necessary.

5.3 Surface protection coatings on LSI composites

Due to the oxidation of carbon above 400 °C, C/C-SiC composites have to be protected with a dense layer providing a low rate of oxygen diffusion into the composite as well as a low rate of carbon diffusion out of the material. To protect the ceramic substrate (Si, SiC) from oxidation and corrosion in combustion environments, e.g. water vapor, an additional environmental barrier coating is needed. The degradation of the composites will be also sharply increased when they are used at temperatures much higher than 1200 °C and or under thermal cycling conditions. Different coatings, which can be applied by chemical vapor deposition (CVD) or vacuum plasma spraying (VPS) were already investigated or are under consideration:

- * *SiC*: CVD-SiC with a thickness of about 50-200 µm can be applied by using trichlorosilane as a precursor. In air a thin silica layer is formed on the top of the CVD-SiC layer, providing oxidation protection at high temperatures. The microcracks will be filled with silica and block the access to oxygen at elevated temperatures > 1100 °C.
- * *BoraSiC*: Multilayer CVD-BoraSiC coating is a three layer coating (SiC-B₂O₃-SiC), which provides an additional self-healing mechanism due the formation of boron oxide at about 900 °C [17, 18].
- * *Yttrium silicates*: Y-silicates are suitable candidates due to their low coefficients of thermal expansion ($4.6-4.8 \cdot 10^{-6} \text{ K}^{-1}$). These coatings show typical thicknesses of 40-150 µm and can be applied through vacuum plasma spraying (VPS) techniques. The suitability of oxidation protection was successfully demonstrated by thermal cycling tests as well as in plasma wind tunnel tests under re-entry conditions [19].

* *Cordierite*: Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) provides an excellent protection in oxidative atmosphere as well as under corrosive conditions. It can be also applied on the surface of LSI composites via VPS with thicknesses ranging from 50-400 μm [20].

* *Pyrocarbon*: Highly pure Pyrocarbon (PyC) coating can be performed by pyrolysis of hydrocarbon gases. This coating exhibits a highly orientated and isotropic structure. It is primarily used for sealing surfaces of graphite and C/C components, which enable a wider use. The sealing prevents the surface from particle release. Furthermore, chemical cannot infiltrate porous structures of graphite and C/C. The compatibility with LSI composites has not already been investigated. Due to the excellent resistance of PyC to liquid salts, which is significantly higher than that of graphite and C/C materials, the components show a higher lifetime in corrosive environments, e.g. if components are in direct contact to salt melts under reducing conditions. Whenever highest purity and/or chemical resistance and/or low particle release are required, a Pyrocarbon coating is the ideal choice.

6 Fields of application for LSI composites to HT (S-I) process

6.1 Tubes for liquid-salt heat transfer

Liquid-salts are known to have the potential to be corrosive, especially when they have impurities and are used at high temperatures up to 1000 °C. It is also known that temperature gradients, which might occur during their heat-transfer lead to mechanical stresses. For this reasons materials with high corrosion resistance, high strength and strain to failure are required.

Tubes fabricated from XB or XT composites might be a good choice for the piping of liquid salts from the nuclear reactor intermediate heat-exchanger to process heat exchangers if they can meet requirements for corrosion and erosion resistance in combination with low permeability. The resistance of these composites can be improved by coating them with Pyrocarbon or CVD-SiC. By this surface modification the wetting behaviour can also be sharply influenced.

The basic manufacture methods for tubes will be based on winding 2D carbon fabrics or preregs on uniform cores. The outer diameters of these cores have to be machined from bulk materials like steel or plastic billets. The preferred technique will be based on autoclave manufacture, since tubes up to a length of some meters might

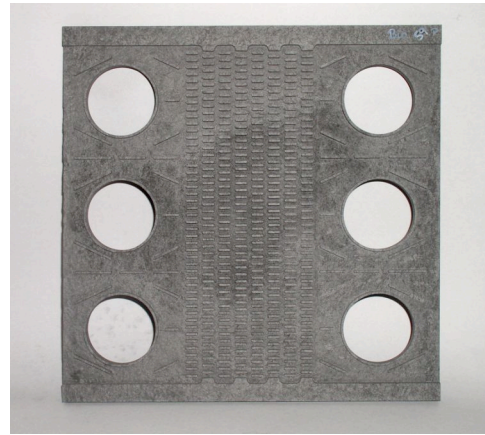
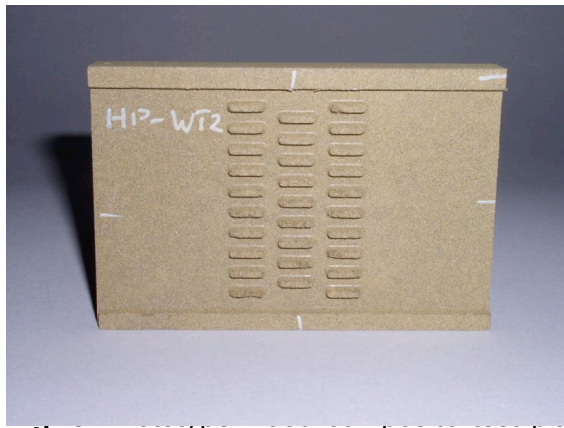
be possible. The RTM technique, already proven for tubes with Ø 50/40 mm and up to lengths of about 850 mm, will be also one possibility for first prototypes but requires a high expense in molds, especially when the diameter of the tubes will be changed. The tube size is then also limited in its diameter and in its length. Different joining designs were already proposed to modify the open ends so that they could be clamped together [16].

6.2 Plate-type heat exchangers

The compact heat exchanger requires a highly gas-tight material. On the other hand the proposed design is based on micro-channels, which are in the mm-scale. For these reasons 2D fibre reinforced LSI composites and even typically short carbon fibres with fibre lengths of about 5-40 mm most likely cannot be used. Such carbon fibres are very stiff and cannot be molded in the desired shape. In addition, the gas permeability of these composites will be too high. Therefore the technical approach must be focused on B1 composite or other commercial SiC ceramics.

DLR proposes a concept using the B1 composite, which contains short carbon fibres, phenolic resin and wood powder. Silicon or SiC powder can be added to reduce the shrinkage and mass loss during pyrolysis. The length of the carbon fibres and grains is preferably less than 1 mm, so that small channels can be created by molding. It is important to maintain a homogeneous mixing of the basic components to obtain a homogeneous material distribution of the single components.

The fabrication of homogeneous net-shape wood based composite (WBC) plates is one of the critical process steps, because all defects will remain in the final ceramic structure. Inhomogenities like closed pores or carbon accumulations will reduce the strength of the composite. Therefore the fabrication of the “green body” must be performed with high accuracy and with high reproducibility. A first prototype with net-shape molded flow channels can be seen in fig. 5, left. Fabrication through molding must be favored, since it is likely to be too expensive to machine carbon bulk material (fig. 5 right). The net-shape fabrication also limits the failure probability, since the machining of porous carbon is expected to cause cracks.



Cardboard prototype (left, 80x120 mm²) with fins (length~ 10 mm). Prototype HX plate (~ 300x300 mm²) in OSF design made from carbon bulk material with high expense in machining. Dimension of fins: 4 mm in height, 2 mm in width, and 10 mm in length (right).

The joining will be preferably done just after molding of the single plates, since then no additional machining is required compared with the joining after the pyrolysis step. The requirements for the joints are that they must be 100 % hermetic, reliable and structurally durable during pyrolysis and final silicon infiltration (fig. 6).

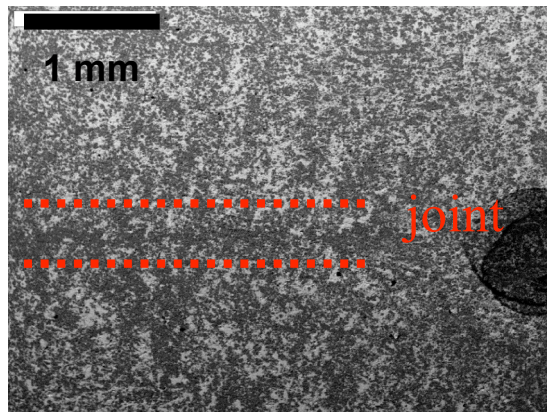
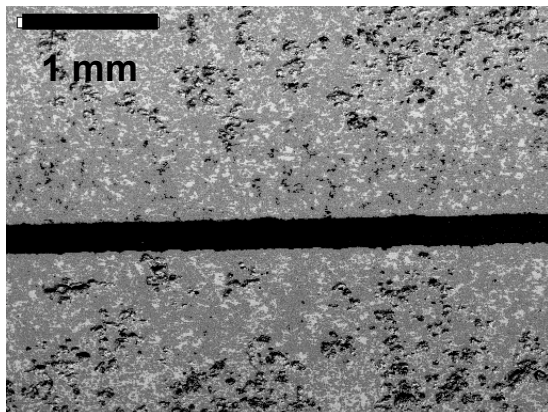


Fig. 6. Joining areas after silicon melt infiltration. Poor joining (left), successful joining with high conversion rate of carbon (right).

Using an OSF design, only a small part of the surface can be used for the single plate joining. These plate areas include the short fins as well as the manifold sections. The total joining surface that can be used will be probably about 50 % of the total surface area. The joining must be performed very accurately. Otherwise the micro-channels will be blocked by the glue. During the pyrolysis the semi-finished compact HX must exhibit very low shrinkage, especially in length and low weight loss

to maintain its structural integrity. During the final in-situ infiltration of the 3D compact with liquid silicon most of the carbon, including the joints, must be converted into SiC and the open porosity ($\varnothing \sim 50 \mu\text{m}$) of the carbon bulk material must be filled with pure silicon. However, all the channels ($\varnothing \sim 1\text{-}2 \text{ mm}$) must remain open. At least three different infiltration methods are known (fig. 7), which can be used for the final silicon infiltration.

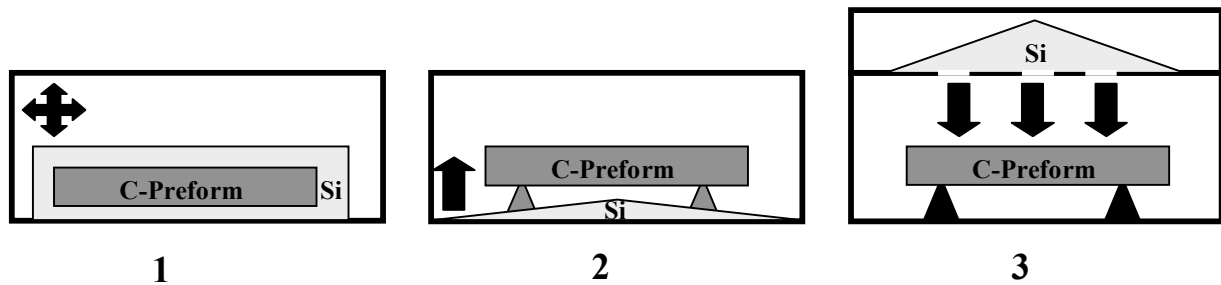


Fig. 7. Methods for pressureless liquid silicon melt infiltration into porous carbon preforms at about 1650 °C. Direct contact method (1), wick method (2), and drop method (3).

If the HX will be used as a chemical reactor for thermal decomposition reactions there will be a strong need to deposit catalysts on some areas of the flow channels, or to insert catalyst-coated granules into the channels. Coatings can probably be applied either during the mixing process of the compounds or after the final Si-infiltration by using CVI methods. The insertion of granules most likely must occur after infiltration, and thus requires attention to the geometry of the flow channels.

An internal coating may be also necessary when molten salts are used as a primary coolant or even to enhance the gas-tightness. In this case Pyrocarbon or CVD-SiC must be applied on the top of the flow channels.

There are still some key challenges to obtain a higher technology readiness level in the fabrication of HX plates based on B1 composite:

- * Improvement of powder mixing and granulation methods to enhance the materials homogeneity, especially in the “green stage”.
- * Accurate net-shape molding of channels/OSF-design by using improved compounds with low viscosity and adapted molding tools.
- * Development of reliable joining methods for net-shape plates (2-10 joinings).
- * Accurate Si-melt infiltration.

- * Refinement of inspections to maintain non-destructive quality assurance (table 4).
- * Fabrication up-scaling to plates/3D stacks with dimensions of about 800-1000 mm.
- * Technology transfer and mass production by an industrial partner.

Table 4. Proposed test methodologies for WBC, porous carbon and ceramics.

	Ultrasonic in air/water	LogIn Thermographie	X-ray	Computer Tomography
WBC plates	X/-			
Carbon plates	X/-			
SiC plates		X	X	X
SiC joinings	-/X			X
3D SiC stack				X

6.3 Acid process vessels and boilers

There is a strong need for novel long-term resistant reactor vessels, boilers or other containers within the hydrogen production plant, since most of the chemical reactants are very corrosive. The needed material have to withstand 800 °C in the gas phase and at least 200 °C in the liquid phase. The final design and dimensions of the production units are not fixed yet and at the earliest will be determined in the next stage after the demonstration of the thermo-chemical pilot plant at in 2007. It is expected that the dimensions may extend up to some meters.

The favourable CFRP fabrication method for large vessels or boilers ($\varnothing > 100$ mm) will be based on the autoclave technique due to the very low expense in molds and easy handling of 2D carbon preregs. Low wall thicknesses ($t < 4$ mm) should be preferred to reduce the danger of debonding during curing and pyrolysis. The strength of such thin walled components could be increased by selecting the XT composite instead of XB type, which shows the highest strength of all proposed composites.

Since all available LSI composites are not 100 % gas-tight and the chemicals are in circulation (flow), there will be a strong need for a surface barrier coating, especially when it is used in gas atmosphere under a certain pressure. For the use in oxidizing atmospheres (e.g. phosphoric acid) SiC will be the most promising coating. For the use at low temperatures (< 450 °C) and non-oxidizing atmospheres (e.g. HI-decomposition, and liquid salts) Pyrocarbon would be also a good choice.

Nevertheless, the gas-tightness of coated LSI composites will be probably limited to low gas pressures and pressure differences.

If complex shaped components in combination with very high gas-tightness are required, the use of B1 composite or commercial SiC must be taken into account. These materials can be machined in the semi-finished C/C or SiC state and then joined prior to the final Si-infiltration or sintering. However, these ceramics are much more brittle than 2D carbon fibre reinforced grades and therefore exhibit only modest thermo-shock resistance.

7 Recommendations for the use of LSI composites

From the proposed LSI materials described in table 1 XB, XT, and B1 will be the most promising candidates in the corrosion environments required for S-I processing. The coupon testing should be done in HI, phosphoric acid, sulphuric acid and liquid salts as can be derived from table 2.

The first test campaign should be concentrated on small test coupons with diameters of $\varnothing \sim 30\text{-}50$ mm. It is proposed to use at least 3 specimens of each type per test, because of the scattering in its composition or inhomogenities, which sometimes occur within LSI composites. The strength, density and porosity of these samples should be determined prior to the testing. The samples should be tested with and without an external coating. Preferred coatings are CVD-SiC and Pyrocarbon. Short-term tests as well as long-term tests, at least up to 1000 hours should be performed. Post-test investigation of the selected materials are recommended, which should determine the changes in microstructure, chemical composition as well as in mechanical strength.

In case that the performance of the LSI composites is sufficient, prototype components should be fabricated and a potentially fabrication for up-scaling should be discussed.

Since there is a great demand for HXs as the key elements for the S-I technology, most of the future work should be concentrated to proof the molding of the proposed flow-channel designs and to scale-up the fabrication to an industrial level. Because the final design is not fixed yet, the investigations should be concentrated on a broad dimensional variety of flow channels as well as on the joining, and accurate Si-infiltration. The optimization of at least 5 process steps, like mixing, molding, joining,

pyrolysis and Si-infiltration is required. It is necessary to perform a two years research program to accomplish a prototype compact HX with the proposed OSF design. The fabrication must be accompanied by leakage tests to proof the gas-tightness of the single layers and the joinings. To show the improvement through the coatings, it also must be shown that CVD-SiC or Pyrocarbon can be applied to the surfaces, including internal flow passages in the HX's.

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